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Separation and determination of the environmental toxic metals using polymer anchored Azomethine complexes

Sreenadha Sarma T[1], **Sreeramulu J**[1], **Siddaiah M**[2]

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Author Affiliation:
[1]Professor, Department of Chemistry, Sri Krishnadevaraya University, Anantapuramu -515003, A.P, India
[2]PRRM College of pharmacy, Kadapa, A.P, India

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ABSTRACT

The effects of Environmental Toxic Metals on human health have long been known and the literature dealing with the subject is immense. The analysis of pollutants by using suitable complexing agent is centered on the development of sensitive technique for detection, determination and remove of contaminants from polluted air, water and land. In view of the importance of Azomethine compounds in pharmaceutical as well as industry, the immobilized polymeric reagents for various analytical analysis, the studies mainly focused on the synthesis of new polymeric reagents for anchoring different Azomethine ligands to polymer matrix. The new polymeric reagents by linking Azomethines to different polymers (Polymer Anchored Azomethines) will be used for Extraction of toxic metal ions (Inorganic pollutants) present in Industrial effluents. The nature and amount can be understood in environmental trace chemistry of pollutants by employing advanced instrumental methods.

Keywords: 4-Morpholinoaniline, vanillin, polymer Schiff base, metal Schiff base complex.

1. INTRODUCTION

A structural study of polymer anchored complexes seems interesting and useful in view of the numerous applications. Anchoring chelating ligands to insoluble polymer matrix and the reaction of these chelating resins with metal ions, metal complexes provide an easy route for the syntheses of immobilized coordination compounds (Gupta et al., 2003; Mannar et al., 2008; Antony et al., 2013; Kuma et al., 2002; Toshishige and Toshiro, 1984; Diether et al., 1986). The Azomethines are important class of ligands which have played a significant role in coordination chemistry and applications of these coordination compounds in various fields (Mannaret al., 2008; Rongmin et al., 2009; Everett and Holm, 1966; Kumar et al., 2013; Radecka et al., 2005) such as Medicinal, Pharmaceutical, Agriculture and Industry. Although a large number of non-Azomethine ligands like diethyl dithio carbamate Radecka et al., (2005), Oxime Haridasan et al., (1987), β – diketones etc (Mansour et al., 2011; Bumagin and Potkin, 2016; Sandra et al., 2005; Thammisetty et al., 2014; Schatz et al., 2010; Shigehisa et al., 2005; Syamal and Singh, 1993) have been immobilized to polymer support, only a few Azomethine have been

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anchored to polymer matrix (Mannar et al., 2008; Kuma et al., 2002; Mansour et al., (2011); Alekha et al., 2013; Shenoy et al., 1984).

The polymer supported reagents are also found important as catalyst, for organic synthesis, trace analysis and environmental applications (Sumitha et al., 2013). For example, ion selective polymer is especially important because of their ability to retain immobilized catalysts, when used as catalyst from their ability to extract targeted metal ions (usually toxic or precious) in the environment or other aqueous media. Representative examples, include amination of chloromethylpolystyrene with 1,3- diamino propane to yield stable resin to complex gold from cyanide solutions (Renata et al., 2005), polymers with dihydroxyl amine acid groups for uranyl ion extraction (Bardaji et al., 2002), polymeric8- hydroxyl quinoline for high copper affinity (Sylwester et al., 2001), a supported quinaidic acid resin for the extraction of cadmium (Samia et al., 2012). A poly (vinyl benzaldoxime) for selective complexation of ferric (Ganjali et al., 2011) (oligomeric sulfide) for high selectivity of mercuric and silver salts (Chanda and Rempel, 1993) and immobilized crown ethers for selective complexation of palladium, gold, silver, mercury salts (Bruening et al., 1991).

Phosphorous based ion exchange resins are often prepared by chemical modification of styrene divinyl benzene copolymers with monophosphate ligands, their complexes have very stability constants with metal ions. For example, methylene diphosphate ligands with polymeric matrix finds applications for the retention and recovery of metal ions from aqueous solution Spiro et al., (1996) therefore they may useful as new series of ion exchange resins with high metal ion affinity. Many toxic metals are present in the polluted water samples. The industrial waste water contains heavy metals are major pollutants. The waste water contains organic, inorganic metals. Thus, may possess a major significant danger to human health. Zinc introduced into water is either remains in dissolved form, which is often used for drinking purposes, so they may be injurious to humans and animals. Many methods have been proposed for their removal forms industrial effluents. The literature survey revealed that there is very little work carried out on the synthesis of di vanillin Schiff base polymer and it is used to remove water soluble Zn (II) ions. Therefore, this investigation has been taken up to go insight in this field and make use of them for environmental pollution analysis and cleaning purpose in industries as well as waste water treatment.

2. MATERIALS AND METHODS

Materials

4-Morpholinoaniline and vanillin are purchased from sigma- Aldrich. Diethyl ether, methanol, Metal salts were purchased from Merck. Analytical grade solvents and chemicals were used throughout the analysis. The IR spectra were record In KBr medium and FTIR Affinity–I techniques on a shimadzu spectrometer in wave number region 4000-400 Cm^{-1} UV spectra were record in Annamacharya pharmacy college, Rajampet, Kadapa. The NMR spectra of the ligand and metal complex were recorded on AV-400 M-HZ NMR spectrometer in IICT, Hyderabad in $CDCl_3$ solvents at room temperature.

Methods

The Polluted water was purified in to different methods. Among all methods ionic exchange method is one of the best methods. Impurities like heavy metal and anions are removed by using polymer exchange resions. Schiff base polymers are used for exchange of heavy metals present in the water. The work on the synthesis of various Azomethines, preparation of metal complexes with metals like Cadmium, Lead, Thallium, Copper, Indium, Palladium, Iron, Manganese, Cobalt having high stability constants which are soluble in water have been carried out. In order to remove these ions waste water and industrial effluents, these should be linked to some polymer matrix for easy separation as insoluble polymeric metal complexes. Azomethines having reactive functional groups OH, NH_2. The ligand and sodium acetate were dissolved separately in ethanol. It was added slowly in to polymer matrix solution. The above solution was stirred at 70^0C for 6 h. The resultant functionalized polymer beads were washed with ethanol and dried.

Method of preparation of Azomethine polymer

Schiff base polymer prepared, equimolar concentrations of 4-Morpholinoaniline and DiVanillin were mixed individually in 50 ml of methanol and refluxed on a water bath with constant starring for about 4 hours. After completion of the reaction, pale yellow substance was obtained. The solid product was filtered off and washed with methanol and distilled water. The crude product was purified by re crystallization in ethanol and the pure Di vanillin Schiff base polymer (DVSP) was obtained. The preparation of the Schiff base polymer equation was represented in Figure-1.

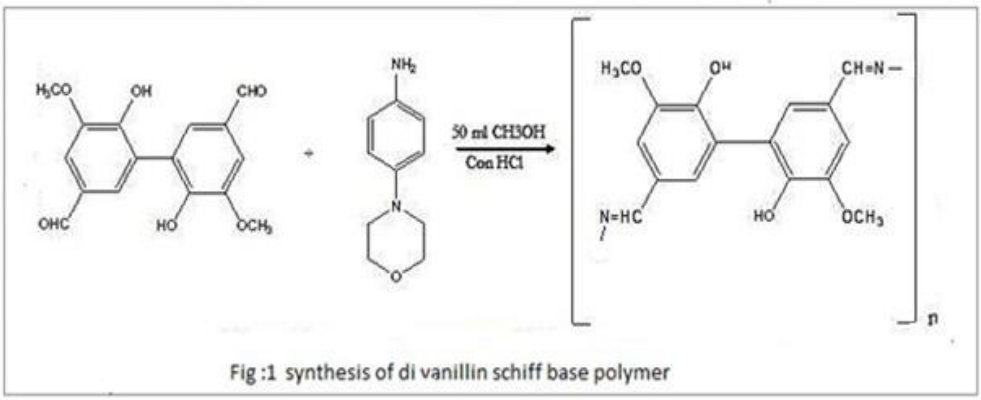

Fig :1 synthesis of di vanillin schiff base polymer

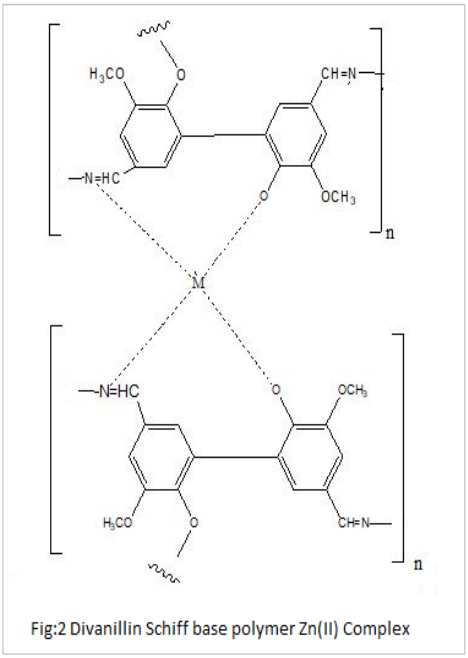

Fig:2 Divanillin Schiff base polymer Zn(II) Complex

Extraction of metal ion in the polluted sample

The functionalized polymer was kept in contact with 100 ml of ethanol. It was added to the polluted water and stirred at 70^0C for 6 h. The crude product was purified by re crystallization in ethanol. The Azomethines as well as the polymers complex will be analyzed by spectroscopic techniques like UV, IR andNMR spectra. The developed new polymeric reagents will be used for extracting the various metal ions present in the waste water and industrial effluents. The metal ions present in the complex can be understood by Electro Analytical Techniques like Polarography, Cyclic Voltammertry. The polymer Schiff base Zn (II) metal complex structure represented in the Figure-2.

Recommended procedure for the removal of metal ions

A stock solution of zinc sulphate used in this study was prepared by dissolving an accurate quantity of zinc sulphate into 100 ml. The polymerized Schiff base was added to zinc sulphate solution and reflected for 6 h**.** The mixture was cooled a precipitate was formed, which was collected by filtration. The compound was re-crystallized with ethanol. The complex was analyzed by using UV, NMR and IR spectroscopy. This data was nearly same that of the above analyzed polluted sample data.

3. RESULTS

The synthesized di vanillin Schiff base polymer was represented in Figure-I and di vanillin Schiff base polymer anchored Zn (II) complex structure was represented in Figure –II. The analyzed data from polluted sample was represented in the Table-I. The IR, UV and NMR specters of polymer Schiff base and polymer anchored Zn (II) discussion was given below.

Table 1 Analyzed data from polluted sample

Inorganic pollutant	Source	Specification limits	Effects
Pb	Automobile Exhaust, Battering, Mixing etc	0.1 ppm	Loss of appetite constipation Abdominal pain
Cd	Soil around steel & Iron works	0.01mg / L	Liver& Kidney damage, acute Gastritis.
Zn	Steel works, edible Oils	5 mg/ L	Dizziness Diarrhea
As	Paper Industry & Cotton growing	0.05ppm	Cramps, paralysis Leukemia
Cr	Metal plating & Wood preservative	0.05 mg / L	Respiratory cancer
Cu	Mining, Metal plating	1.5 ppm	Essential Trace Elements, Toxic to plants
Mn	MiningWastes	0.05 mg / L	Highly Toxic

4. DISCUSSION

The synthesized Di vanillin Schiff base polymer was yellow in colour and melting point 172-174^{0}c. The schiff base polymer was insoluble in water. Infrared spectra of di vanillin Schiff base polymer and polymer anchored Zn (II) complexes were recorded with FTIR Affinity-I techniques on a shimadzu spectrometerin wave number region 4000-400 cm^{-1} using KBr pellets. The IR spectra of polymer Schiff base Zn (II) complex was compared with the ligand indicate the intraction of coordination sits with the metal ion. The FTIR spectra of the polymer Schiff base ligand gave a strong band at 1635 cm^{-1}, due to the formation of Schiff base. This band was shifted to a 1624 cm^{-1}in the metal complex, indicating Azomethine of nitrogen was involved in the bond formation with metal. The new band was obtaining the 737 cm^{-1} region, indicating the formation metal–nitrogen bond. In the polymer Schiff base Zn (II) another new band was obtain the 619 cm^{-1}, indicating formation of a metal–oxygen bond. The^{1}H NMR of polymer schiff base and polymer schiff base Zn (II) complex was measured in $CDCl_3$ as solvents. The^{1}H NMR of polymer Schiff base ligand δ (ppm): 8.38 (s, 1H, CH=N, Azomethine), 6.93-7.19 (Ar-H, aromatic protons), 3.87 (S, 3H, -OCH_3), 5.94 (S 1H,-OH). The^{1}H NMR of polymer schiff base Zn (II) complex δ (ppm): 8.65 (s, 1H, CH=N, Azomethine), 6.98-7.30 (Ar-H, aromatic protons), 3.95 (S, 3H, -OCH_3). The polymer Schiff base Zn (II) complex was diamagnetic as expected ford^{10} systems. The electronic spectrum shows no bands and the complex may be assigned a tetrahedral geometry. The polymer anchored complex was insoluble in common organic solvents.

5. CONCLUSION

In view of the importance of Azomethine compounds in pharmaceutical as well as industry, the immobilized polymeric reagents for various analytical analysis, this work has been taken up to synthesize new polymeric reagent, by anchoring different Azomethine ligands to polymer matrix for the analysis of metal ions in the industrial effluents, for water analysis and treatment of polluted water to use for environmental pollution control measures. The literature survey revealed that there is little work carried out on the synthesis of polymeric Azomethine ligands. Polymer Schiff base system seems to have very efficient and economical for removing toxic metals from industrial waste water.

Summary of research

The synthesized polymer Schiff base ligand was developed as a reagent for removal of Zn (II) form solution. The remove of Zinc from the waste water increases with increasing contact time. The relative increase in the extent of removal of metal ion from the waste water up to some extent of time after the removal of metal ion from the waste water was constant. Hence the optimum time of reflux was fixed. This polymer Schiff base and metal complex was further useful for bacterial activities.

Future issues

This method was the most important advantage method to removing of metal ions in the waste water up to the maximum.

Abbreviations

DVSP = Di vanillin Schiff base polymer

Disclosure statement

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Ethical approval

Not applicable.

Informed consent

Not applicable.

Conflicts of interests

The authors declare that there are no conflicts of interests.

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Data and materials availability

All data associated with this study are present in the paper.

REFERENCES AND NOTES

1. Alekha KS, Yasobanta Das, Sasmita Pattnaik, Nibedita Nath, Prasanta Rath, Tungabidya Maharana. Int J Mater Sci Appl 2013; 2:136-145.
2. Antony R, Theodore S, Saravanan K, Karuppasamy K, Balakumara S. Synthesis, spectroscopic and catalytic studies of Cu(II), Co(II) and Ni(II) complexes immobilized on Schiff base modified chitosan. J Mol Struct 2013; 1050:53-60.
3. Bardaji M, Laguna A, Reyes PM. Unexpected Ring-Opening Reaction to a New Cyanamide-Thiolate Ligand Stabilized as a Dinuclear Gold Complex. Organometallics 2002; 21:1877–188 1.
4. Bruening RL, Tarbet BJ, Krakowiak KE, Brucning ML, Izatt RM, Bradshaw. Quantitation of cation binding by silica gel bound thiamacrocycles and the design of highly selective concentration and purification columns for palladium (II), gold (III), silver (I), and mercury (II). Anal Chem 1991; 63:101 4-1017.
5. Bumagin NA, Potkin VI. Functionalized isoxazole and isothiazole ligands: Design, synthesis, palladium complexes, homogeneous and heterogeneous catalysis in aqueous media. Russ Chem Bull 2016; 65:321–332.
6. Chanda M, Rempel GL. Selective sorption of ferric ion onto cross linked poly (vinylbenzaldoxime). React Funct Polym 1993; 19: 201-212.
7. Diether Wohrle, Heike Bohlen, Johannesk Blum. Polymeric Schiff base chelates and their precursors. Synthesis of covalently and coordinatively bound polymeric chelates and their dioxygen binding in the solid state. Macromol Chem Phys 1986; 187:2081–2096.
8. Everett GW, Holm RH. Studies of the Planar-Tetrahedral Configurational Equilibrium of Bis (β-Ketoamino) Cobalt (II) Complexes. J Am Chem Soc 1966; 88:2442-2451.
9. Ganjali H, Ganjali MR, Alizadeh T, Faridbod F, Norouzi P. Bio-Mimetic Cadmium Ion Imprinted Polymer Based Potentiometric Nano-Composite Sensor. Int J Electrochem Sci 2011; 6:6085–6093.
10. Gupta KC, Abdulkadadir HK, Chand S. Polymer-immobilized N, N'bis (acetylacetone) ethylenediamine cobalt (II) Schiff base complex and its catalytic activity in comparison with that of its homogenized analogue 2003; 90:1398-1411.
11. Haridasan VK, Ajayaghosh A, Ajasekharapillai VN. Polymer-bound mixed carboxylic dithiocarbamic anhydrides. A new class of selective and recyclable solid-phase acylating reagents. J Org Chem 1987; 53:2662–2665.
12. Kuma D, Gupta PK, Syamal A. Synthesis and characterization of poly styrene supported Coordination compounds of dibasic tridentate Schiff base. Int J Chem 2002; 41:2494-2499.
13. Kumar D, Syamal A, Sharma LK. Synthesis, magnetic and spectral studies on polystyrene-anchored coordination complexes of bi-, tri-, tetra- and hexavalent metal ions with unsymmetrical dibasic tetradentate onno donor schiff base derived from 3-formylsalicylic acid, ethylenediamine and 2-

hydroxy-1-naphthaldehyde. J Appl Chem 2013; 54:12593-12597.

14. Mannar R Maurya, Aarti Arya, Pedro Adao, Joao Costa pessoa. Immobilisation of oxovanadium (IV), dioxomolybdenum(VI) and copper(II) complexes on polymers for the oxidation of styrene, cyclohexene and ethylbenzene. Appl Catal 2008; 351:239-252.
15. Mansour Arab Chamjangali, Ghadmali Bagherian, Ali Mokhlesian, Bahram Bahramin. Synthesis and application of chloromethylated polystyrene modified with 1-phenyl-1, 2-propanedione-2-oxime thiosemicarbazone (PPDOT) as a new sorbent for the on-line preconcentration and determination of copper in water, soil and food samples by FAAS. J Hazard Mater 2011; 192:1641-1649.
16. Radecka–paryzek W, Violetta patroniak, Jerzy lisowsk. Metal complexes of polyaza and polyoxaaza Schiff base macrocycles. Coord Chem Rev 2005; 249:2156-2175.
17. Renata Drozdzak, Bart Allaert, Nele Ledoun, Ileana Dragutan, Valerian Dragutan, Francis Verpoort. Synthesis of Schiff base –Ruthenium complexes and their applications in catalytic process. Adv Synth Catal 2005; 347:1721-1743.
18. Rongmin YU, Xiao-Feikuang, Xiao-Yuan Wu, can-Zhonglu, james Donahue P. Stabilization and immobilization of polyoxometalates in porous coordination polymers through host–guest interactions. Coord Chem Rev 2009; 253:2872-2890.
19. Samia A Kosa,Ghalia Al–Zhrani, Mohamed Abdel salem. Removal of heavy metals from aqueous solutions by multi-walled carbon nano tubes modified with 8-hydroxyquinoline. Chem Eng J 2012; 181:159-168.
20. Sandra G, Jose A, Fermandes Rainho P, Rute A, Teresa M, Paulo JA, Isabel S. Highly Luminescent Tris (β-diketonate) europium(III) Complexes Immobilized in a Functionalized Mesoporous Silica. Chem Mater 2005; 17:5077–5084.
21. Schatz A, Toby Long R, Robert N, Grass WJ, Stark HR, Resiser O. Immobilization on a Nanomagnetic Co/C Surface Using ROM Polymerization. Generation of a Hybrid Material as Support for a Recyclable Palladium Catalyst. Adv Funct Mater 2010; 20:4323-4328.
22. Shenoy AV, Saini DR, Nadkarni VM. Melt Rheology of Polymer Blends from Melt Flow Index; Int J Polym Mater 1984; 10:213-235.
23. Shigehisa, Akine, Takanori, Wenkuri Dong, Sayuri Masubuchi, Nabeshima Tatsuya. Oxime-Based Salen-Type Tetradentate Ligands with High Stability against Imine Metathesis Reaction. J Org Chem 2005; 70:1704-1711.
24. Sprio D, Alexandratos Andrzej, Trochimezerk W, Crick EW, Phillip HR, Gatnone C, Renato Chairizia. Macro molecules, Synthesis and Ion–complexing properties of a Noval polymer –supported Reagent with Diphosponate ligands. Micro molecules 1996; 29:1021-1026.
25. Sumitha Roy, Chatterajee T, Manirul Islam SK. Polymer anchored Cu (II) complex: An efficient and recyclable catalytic system for the one-pot synthesis of 1, 4-disubstituted 1, 2, 3-triazoles starting from anilines in water. Green Chem 2013; 9.
26. Syamal A, Singh MM. Syntheses and characterization of new cobalt (II) complexes of polystyrene-supported resin containing the Schiff bases derived from 3-formylsalicylic acid and 2-aminophenol, 2-aminobenzyl alcohol or 2-hydroxybenzylamine. React Funct Polym 1993; 21:45-52.
27. Sylwester ER, Allen PG, Dharmawardana UR, Sutton M. Structural Studies of Uranium and Thorium Complexes with 4, 5-Dihydroxy-3, 5-benzenesdisulfonate at Low and Neutral pH by X-ray Absorption Spectroscopy. Inorg Chem 2001; 40:2835-2841.
28. Thammisetty RS, Kesavulu K, Peddakotla VR. Synthesis, characterization and applications of polymer-metal chelates derived from poly [((4-acryloxy acetophenone)-divinylbenzene)] benzoyl hydrazone resins. Chem Sci J 2014; 126: 597–608.
29. Toshishige MS, Toshiro Yokoyama. Preparation and complextion preparation of polystyrene resins containing diethylene triamine derivatives. Polyhedron 1984; 3:939-945.